

Ising pyrochlore magnets: Low temperature properties, ice rules and beyond

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Pyrochlore magnets are candidates for spin-ice behavior. We present theoretical simulations of relevance for the pyrochlore family $R_2\text{Ti}_2\text{O}_7$ (R = rare earth) supported by magnetothermal measurements on selected systems. By considering long ranged dipole-dipole as well as short-ranged superexchange interactions we get three distinct behaviours: (i) an ordered doubly degenerate state, (ii) a highly disordered state with a broad transition to paramagnetism, (iii) a partially ordered state with a sharp transition to paramagnetism. Thus these competing interactions can induce behaviour very different from conventional “spin ice”. Closely corresponding behaviour is seen in the real compounds—in particular $\text{Ho}_2\text{Ti}_2\text{O}_7$ corresponds to case (iii) which has not been discussed before, rather than (ii) as suggested earlier.

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The pyrochlore rare earth titanates have attracted great attention recently because their unusual structure (the “pyrochlore lattice”) of corner-sharing tetrahedra can lead to geometric frustration and interesting low-temperature properties [1]. Our interest in these particular titanates was sparked by the observation (confirmed by our crystal field calculations) that some of them are nearly ideal Ising systems [2–4]. Some intriguing experimental data presented below can only be explained by assuming a competition between classical dipole-dipole interactions and quantum superexchange. Depending on their relative magnitudes, the ground states of the Ising-like systems can be “ice-like”, ordered, or partially ordered. “Ice models” get their name because real (water) ice [5] has a large ground state degeneracy arising from local rules for the ordering of protons in water ice. Several related models have been studied since, but as far as we know this is the first time that two competing interactions have been included in such a model, with the physics changing significantly depending on their relative strengths.

Pyrochlores of the form $A_2B_2O_7$ have been extensively studied, where A are rare earth ions and B are transition metal ions, each forming interpenetrating pyrochlore lattices. Often these can be modelled by isotropic Heisenberg antiferromagnets because the B atom is magnetic ($B = \text{Mn}, \text{Mo}$) [6–8] with a small dipole moment, and the A atom is nonmagnetic (eg $A = \text{Y}$), so the dominant interaction between the B atoms is superexchange. The lattice is a three dimensional version of the kagomé lattice, with a parallelepiped as the unit cell and a tetrahedron as the basis (figure 1). Typically the magnetic ions sit at the corners of these tetrahedra. The tetrahedra form a face centred cubic lattice, so the structure can be viewed as four interpenetrating fcc lattices and the unit cell is often pictured as a cube, but we used the smaller parallelepiped unit cell in our simulations. The lattice can exhibit frustration; in the isotropic Heisenberg case, this happens for the antiferromagnet [7,9,10], but in an Ising limit it can happen even with ferromagnetic interactions [2–4].

In our systems, the Ti^{4+} , like the O^{2-} ions, are nonmagnetic and play no role apart from holding the lattice together. However, typically the rare earth ion carries a large magnetic moment (from its unfilled f -electron shells), so that the dipolar interaction is as significant as the superexchange. Another important aspect is the single ion anisotropy imposed by the crystal field (CF) interaction of D_{3d} symmetry at the rare earth site, since a strong easy-axis anisotropy results in the Ising limit, even for isotropic exchange interactions. Previous investigations of the low-temperature properties of these systems assumed a strong single-ion anisotropy along the $\langle 111 \rangle$ direction, i.e. along the line pointing from the center of the tetrahedron to the corner where the rare earth is located [2,11] However, there is so far no direct experimental evidence to support this assumption. We have therefore investigated in detail the CF interaction in the Ho-compound using inelastic neutron scattering [12].

From the energies and intensities of the observed CF transitions, we could unambiguously determine the CF parameters and energy levels of $\text{Ho}_2\text{Ti}_2\text{O}_7$ (top inset to fig. 1). Because the crystal structure varies very little on replacing one rare-earth ion by another, these CF parameters will give good estimates of the splitting and single ion anisotropy in the other compounds as well. So we find a strong easy-axis anisotropy along the line joining the tetrahedra centres for Ho and Dy, but not for Yb, Er or Tb.

Though it has been suggested earlier [2,11] that $\text{Yb}_2\text{Ti}_2\text{O}_7$ is also Ising like, we find that there is in fact an easy plane here, rather than an easy axis: $J = 7/2$, $J_z = \pm 1/2$ for the ground states, so the spin points mainly in the x - y

plane. The same seems to be true for Er, while Tb may be Ising like but only at very low temperatures (< 0.1 K).

The nearest-neighbour Ising model on this lattice (considered in [2–4]) can show at most two kinds of behaviour depending on the sign of the interaction. If the interaction is “antiferromagnetic”, the ground state is doubly degenerate and each tetrahedron has alternately all spins pointing out or all spins pointing in. If the interaction is “ferromagnetic”, the ground state of a tetrahedron is given by an “ice rule” where two spins point out and two into the tetrahedron, and is sixfold degenerate. Any state with all tetrahedra satisfying this is a ground state. It is highly degenerate with a finite entropy per spin, which our simulations suggest is around $0.22 k_B$ in agreement with Pauling’s prediction [13]. In both cases, the specific heat vanishes at small as well as large temperatures, with a peak in the middle. Simulations show that in the ferromagnetic case (ice rule) the peak is broad, and occurs at the temperature scale of the interaction, suggesting a typical broad crossover from a glassy low-temperature phase with macroscopic entropy to a paramagnetic phase. In the antiferromagnetic case, the peak is very sharp and is at a temperature around 4 times the interaction energy, suggesting a phase transition from an ordered ground state to the paramagnetic phase. The energy scale of the peak here may be higher because the energy cost of a single spin flip from the ground state is 12 times the interaction energy of a pair of dipoles, as opposed to four times this energy in the ferromagnetic case.

Experiments were done on polycrystalline samples of these compounds which were synthesized from stoichiometric mixtures of the lanthanide oxides (99.99%) and TiO_2 (99.995%) heated at 1200°C in air for 1 week with intermediate grindings. All materials were found to be phase pure by conventional powder X-ray diffraction. The specific heat was determined using a standard semiadiabatic technique, and the susceptibility measured with a commercial magnetometer. All susceptibility data were taken at 0.1 Tesla.

While simulations for the specific heat of the nearest neighbour model suggest a broad crossover (antiferromagnetic interaction) or a sharp narrow peak (ferromagnetic), for Ho something entirely different occurs: at around 0.6 K a transition seems to occur, below which the spins seem to decouple thermally from the system and freeze out into a low temperature metastable glassy phase. Moreover, the data for Ho suggests a peak at substantially smaller energies than the dipolar interaction (2.3 K). To explain this we need to go beyond the nearest neighbour model, by (a) considering the long-ranged dipole-dipole interaction between the spins, (b) including an antiferromagnetic superexchange to reduce the dipolar coupling.

It turns out that the Dy compound is very well described by a purely dipole-dipole interaction but with a reduced effective dipole moment (around 75% of the full value). This could be explained by a superexchange which falls off for the nearest few neighbours in roughly the same way as the dipolar interaction. This compound is very interesting in its own right, being a good realization of the “ice models” which have interested physicists for a long time, and we have discussed it extensively elsewhere [14].

The fact that Ho has significantly different behaviour from Dy means that the superexchange behaves differently. It is not possible to account for this cleanly, so we merely assume that the superexchange is nearest-neighbour only: this still gives us excellent agreement with the observations and highlights why these compounds are different from “spin ice”. We calculate the dipole-dipole interaction, assume a nearest-neighbour superexchange which we estimate from the experimental data, do a simulation for the specific heat and susceptibility with these values, and compare with experiment. Our simulations are on systems with 2048 spins ($8 \times 8 \times 8$ tetrahedra each with 4 sites) and around 10000 Monte Carlo steps per spin. We use a long-ranged dipole-dipole interaction (up to 5 nearest neighbour distances, but the results don’t change significantly beyond the third neighbour). The convergence is good despite the long range of the interaction, probably because there is no global Ising axis and no net magnetization, so beyond the third neighbour the large numbers of spins in different directions tend to cancel one another.

We obtain the superexchange for Ho from the experimental high temperature zero field susceptibility. The high temperature expansion of the susceptibility is readily obtained from elementary statistical mechanics. First we fix the notation: We use scalar Ising spins, $S_i = \pm 1$, with $S_i = +1$ if it points out of an “upward” tetrahedron (or, equivalently, into a “downward” tetrahedron) and $S_i = -1$ otherwise. We write the first two terms in the expansion as $\chi(T) = \frac{C_1}{T} (1 + \frac{C_2}{T})$ and try to evaluate these coefficients using $M = \frac{1}{N} g_s \mu_B \langle \sum_i S_i \cos \theta_i \rangle$ where g_s is the Lande factor, S_i is the effective spin of rare earth atom i ($= \pm |J_z|$ for that atom), μ_B is the Bohr magneton, and θ is the angle made by the direction of the spin with the (arbitrarily chosen) direction of the external magnetic field. Our results turn out to be independent of the direction, at least to this order. The angle brackets denote the thermodynamic average. From the fluctuation-dissipation theorem, $\chi(T) = \frac{1}{N} \beta (g_s \mu_B)^2 \sum_{i,j} \Gamma_{ij}$ where $\Gamma_{ij} = \langle S_i \cos \theta_i S_j \cos \theta_j \rangle_{\mathcal{H}=0}$. Using standard methods (expanding to order β), we arrive at

$$\chi(T) = \frac{N(g_s \mu_B)^2 S^2}{k_B T} \frac{1}{3} \left[1 - \frac{6S^2}{k_B T} \frac{1}{4} \sum_{\substack{i \\ \text{over 1} \\ \text{tetrahedron}}} \sum_j J_{ij} \cos \theta_i \cos \theta_j \right]$$

The sum over j is over all sites in the lattice excluding i . If the nearest-neighbour dipolar interaction is J_D , the superexchange is J_S , and we include long-ranged dipolar interaction but only nearest neighbour superexchange, we get

$$\chi(T) = \frac{N(g_s\mu_B)^2}{k_B T} \frac{S^2}{3} \left[1 + \frac{6S^2}{k_B T} \frac{1}{4} (2.18J_D + 2.67J_S) \right]$$

and from here we can extract the coefficients C_1 and C_2 .

This is valid for an ideal Ising model at sufficiently high temperatures. When we plot the experimental χT against $1/T$ (Fig. 2), we find a marked linear region at low temperatures (2–10 K). This is the region we want: if we pull out C_2 from this region, we find it is much less than 1 K, so things are consistent. At higher temperatures, where the Ising approximation should fail, the graph is no longer linear. We equate this value of C_2 to $(6S^2/4)(2.18J_D + 2.67J_S)$ with J_D known, pull out J_S , and do the simulation. In fact, since the slope is so small, the error is not too great if we simply put $C_2 = 0$. But using the measured slope of C_2 (and using the calculated value of C_1 , for consistency, rather than the fitted value) we get $J_D = 2.35$ K (calculated) and $J_S = -1.92$ K (measured), both for the Ho and the Dy compounds. (Note that when we use scalar Ising spins rather than fixed vector spins, the superexchange is *negative* and the dipolar J is *positive*—and the former favours ordering, the latter frustration, as is usually the case in Ising systems.)

We now simulate with these values of J_D and J_S . In the case of $\text{Ho}_2\text{Ti}_2\text{O}_7$ (Fig. 3), the simulated susceptibility agrees well with the experimental data at all temperatures, while the specific heat has a sharp peak at very nearly the point where the experimental Ho system falls out of thermal equilibrium. Moreover, there is a large energy difference at this point, suggesting a first-order phase transition.

The Yb compound has earlier been believed to be an Ising model, and we initially tried modelling it in this way, with a nearest-neighbour antiferromagnetic superexchange. The experimental data show a sharp peak, which is as we expect for an antiferromagnetic Ising model, and matching the position of the peak in the simulation in the observed position leads to fair agreement with experiment (fig. 3). This should be regarded as fortuitous. The neutron data suggest that the Yb and Er compounds are easy-plane (“XY models”), not Ising. Earlier work by Bramwell *et al.* [15] suggests that the XY Heisenberg model on this lattice shows a first order phase transition from an ordered ground state; we believe that, as with $\text{Ho}_2\text{Ti}_2\text{O}_7$, it may be necessary to include a dipole-dipole interaction, and preliminary simulation of a pure dipole model correctly predicts the position and approximate shape of the peak. More work on this is in progress. Our specific heat measurements on Er and Yb agree with previous data [11].

The remaining compound, $\text{Tb}_2\text{Ti}_2\text{O}_7$, is probably Ising-like at very low temperatures. It has been suggested that it remains paramagnetic down to 0.07 K [16]. The gap to the excited CF states is only a few kelvin. The data for this and Er are shown in fig. 4, but no simulations were done for these.

The ground states of nearest-neighbour ferromagnetic or antiferromagnetic Ising pyrochlores are well known; we now consider the more complicated case of $\text{Ho}_2\text{Ti}_2\text{O}_7$. In the nearest neighbour ferromagnetic model any state in which all tetrahedra satisfy the “ice rule” will be a ground state. With long-ranged interactions ($\text{Ho}_2\text{Ti}_2\text{O}_7$), the ice rule remains but there are further restrictions on the allowed ground states. One way to deal with these restrictions is to consider the system as a set of interacting “upward” tetrahedra, assign ice rules to the configurations of each, and determine what configuration of neighbouring tetrahedra will lower the energy. There should be an ice rule for the “downward” tetrahedra, but also other constraints. This will map on to a new interacting lattice system, with a six valued variable at each lattice site representing the configuration of the upward tetrahedron represented by that lattice site.

This approach for Ho, and the simulation, suggest a partial ordering in the ground state. That is, the upward tetrahedra could have one of two allowed configurations; the configuration varies randomly along one lattice direction, but alternates perfectly along the other two. So the number of ground states is large but not macroscopic (it is exponential in L , the system length, rather than L^3), and the entropy per particle vanishes. Our calculation here ignored long-ranged superexchange, and thus may not be valid for the experimental system, but the experimental data for Ho do suggest a vanishing entropy for the ground state (on integrating C/T). In the simulation, the system remains in a disordered “paramagnetic” state till the transition temperature, but below this temperature it freezes out rapidly to such a partially ordered state. From then on further cooling leaves it stuck in this state, with the other ground states inaccessible. This seems to agree with the observation that the spins freeze in $\text{Ho}_2\text{Ti}_2\text{O}_7$ below a temperature of around 0.6 K. Below this temperature inability to establish thermal equilibrium leads to unreliable data, which has not been plotted here.

The freezing of spins is an interesting phenomenon in $\text{Ho}_2\text{Ti}_2\text{O}_7$. We believe it is because at the transition temperature (0.8 K) the single spin flip energy is around 4 K, so the Boltzmann factor for this is very small (around 0.006).

A single spin flip from the ordered ground state for Yb has a much larger Boltzmann factor of 0.05 (assuming only near-neighbour interaction), so the fall in specific heat is not so sharp. This “spin freezing” in $\text{Ho}_2\text{Ti}_2\text{O}_7$ has been commented on by Harris *et al.*. It seems the next-neighbour interactions must be fairly strong for this. In the absence of next-neighbour interactions there is a very large number of ground states. As we turn on and increase the next-neighbour interaction, the new constraints substantially reduce the ground state entropy. For a pure dipole-dipole interaction the new ground state entropy is reduced but still finite, but with large superexchange, as in $\text{Ho}_2\text{Ti}_2\text{O}_7$, it actually vanishes: there are few true ground states, and these are separated by large energy barriers.

In summary, we perform simulations based on a theoretical calculation of dipole-dipole interactions and an estimated superexchange obtained from the experimental data. The relative strengths of these interactions have a drastic effect on the ground state properties when compared to a nearest-neighbour Ising model, and we observe three different kinds of ground states: highly disordered and ice-like [14], partially ordered, or fully ordered, with broad crossovers or sharp phase transitions to high temperature phases. We use only one adjustable parameter, fitted from the experimental data, as input for the simulations that agree well with experiment. Thus these systems look like excellent testing grounds to study the behaviour of disordered spin systems, glassy dynamics, and phase transitions, with the opportunity to tune the interactions to some extent, and should richly repay future study.

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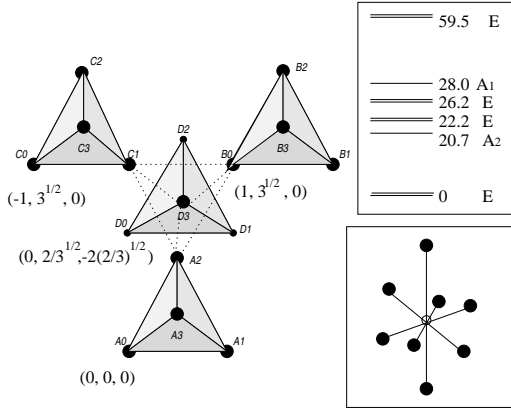


FIG. 1. The basis of atoms $A0 = (0, 0, 0)$, $A1 = (r, 0, 0)$, $A2 = r(1/2, \sqrt{3}/2, 0)$, $A3 = r(1/2, 1/[2\sqrt{3}], \sqrt{2/3})$; translated by the lattice vectors $\mathbf{a}_1 = (r, \sqrt{3}r, 0)$, $\mathbf{a}_2 = (-r, \sqrt{3}r, 0)$, $\mathbf{a}_3 = (0, 2r/\sqrt{3}, -2r\sqrt{2/3})$ to form tetrahedra B , C and D ; repeated translation forms the whole lattice. In our systems, $r = 3.53\text{\AA}$. We can also choose a basis of “downward” tetrahedra (dotted lines; atoms $A2$, $B0$, $C1$, $D3$). (*inset bottom*) A single rare earth ion (centre) surrounded by eight oxygen ions. The top two are at the centres of the tetrahedra adjacent to the rare earth ion, and the rest form a puckered hexagonal ring around this axis. (*inset top*) The first few calculated energy levels for Ho, in meV, with symmetry indicated. Ground state transitions are observed at 22, 26, 59, 71 and 77 meV (last two not shown).

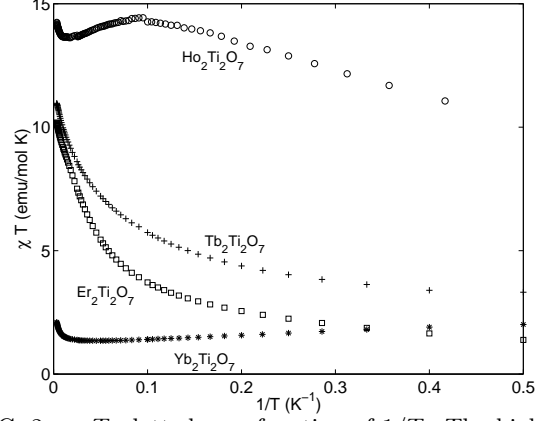


FIG. 2. χT plotted as a function of $1/T$. The high temperature expansion in the text is the markedly linear low temperature region here (2–10 K, which is high compared to C_2). Note that the Yb compound has the opposite slope here from Ho, suggesting that superexchange dominates here.

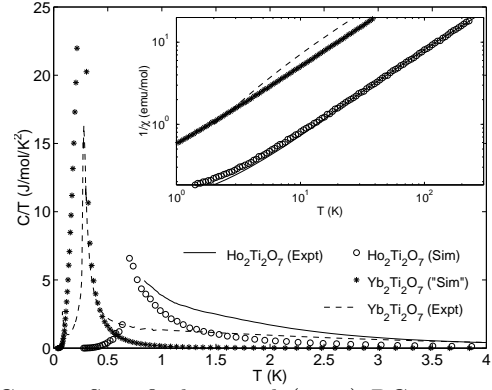


FIG. 3. Specific heat and (inset) DC susceptibility for $\text{Ho}_2\text{Ti}_2\text{O}_7$ and $\text{Yb}_2\text{Ti}_2\text{O}_7$. The Yb “simulation” here is for an Ising model, which is probably inappropriate but gives fair agreement.

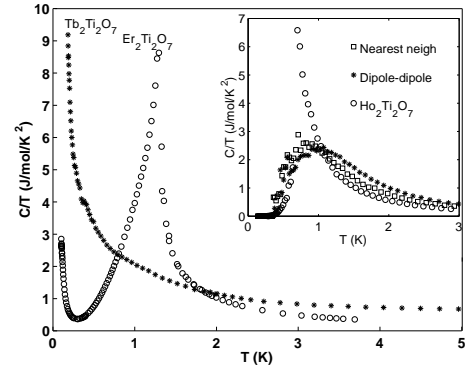


FIG. 4. The measured specific heat for $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Er}_2\text{Ti}_2\text{O}_7$, and (inset) a comparison of three simulations for the specific heat: the nearest neighbour dipolar interaction, the long ranged dipolar interaction, and the long-ranged dipolar interaction modified by a nearest neighbour superexchange (which we use for the Ho compound). The third case is very different from the first two.